INTERNATIONAL JOURNAL OF AGRICULTURE & BIOLOGY
ISSN Print: 1560–8530; ISSN Online: 1814–9596
15–111/2016/18–1–52–60
DOI: 10.17957/IJAB/15.0061
http://www.fspublishers.org

Full Length Article

Application of Raw and Composted Recycled Paper Mill Sludge on the Growth of *Khaya senegalensis* and their Effects on Soil Nutrients and Heavy Metals

Rosazlin Abdullah[1*], Che Fauziah Ishak[2], Wan Rasidah Kadir[3] and Rosenani Abu Bakar[2]
[1]*Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603. Kuala Lumpur, Malaysia*
[2]*Department of Land Management, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia*
[3]*Soil Management Branch, Forest Research Institute Malaysia, 52109 Kepong, Selangor Darul Ehsan, Malaysia*
*For Correspondence: rosazlin@um.edu.my

Abstract

The paper industry performs an essential role in the global economy of the world. A study was conducted on the paper mill sludge that is applied on the *Khaya senegalensis* for 4 crop cycle for 1 year growth at glasshouse, Faculty of Agriculture, Universiti Putra Malaysia. Paper Mill Sludge (PMS) and composted Recycled Paper Mill Sludge (RPMS) was used with nitrogen (0, 150, 300 and 600 kg ha^{-1}) at the ratio of 1:1 (Recycled Paper Mill Sludge (RPMS): Empty Fruit Bunch (EFB). The growth parameters were measured twice a month for 6 months. Plant nutrients and heavy metal uptake were determined. The paper mill sludge has the potential to be a supplementary N fertilizer as well as a soil amendment. The application of RPMS with N, significantly contributed to the improvement in plant growth parameters such as plant height (193 cm), basal diameter (27.00 mm), total plant biomass and improved soil physical and chemical properties. Total concentrations of heavy metals in soils were below the critical values. Hence, the paper mill sludge can be successfully used as soil amendment in acidic soil without any serious threat. The use of paper mill sludge for soil fertility, shows improvement in land application and signifies a unique opportunity to recycle sludge back to the land to alleviate the potential waste management problem.

Keywords: Growth; Heavy metals; Nutrient uptake; Production; Waste management

Introduction

The waste paper sludge is a growing problem worldwide and subsequently sludge production will continue to increase and environmental quality standards will become more stringent. Global production in the pulp and paper industries is expected to increase by 77% by the year 2020 with over 66% of paper will be recycled at the same time (Lacour, 2005). On an average, the majority of waste generated from paper production and recycling is from paper mill sludge, which is a by-product of up to 23.4% per unit of producing paper (Miner, 1991). In Malaysia, there are 67 paper mills producing more than 50 tons of paper per day (any kind of traditional, recycled and special papers), of which 19 are small paper manufacturing companies using wood fiber, which includes integrated pulp and is located at Sipitang, Sabah (Sabah Forest Industries). The Malaysia pulp and paper industry is mainly dependent on important fiber, particularly virgin pulp, whereas the recycled paper is used as a source of feed stock in Malaysia (Jean and Santosh, 2006).

The commercial use of paper mill sludge as fertilizer and soil amendment in Malaysia is still at the infancy stage. As the paper mill industries in Malaysia continue to expand, the production of paper mill sludge will increase as well. Utilization of organic by-products as soil amendments in agricultural production exemplifies a strategy for converting waste to resources. Utilization of recycled paper mill sludge from the paper industry seems to have the potential to enhance long-term fertility to cultivated soils due to its ability to provide added benefits to supply both organic matter and nutrients for crop growth. Application of these wastes will improve soil fertility and encourage waste reutilization and thus, may also reduce both the treatment and disposal costs. In order to make pulp sludge recycling as a viable option form paper mills, it must demonstrate that the waste has the ability to increase crops' growth performance. Several studies have been conducted which documented the effects of pulp sludge on crop yield and soil fertility in land application scenarios (Vasconcelos and Cabral, 1993; Catricala *et al*., 1996). The appropriate organic amended management can potentially increase the

To cite this paper: Rosazlin, A., C.I. Fauziah, W.K. Rasidah and A.B. Rosenani, 2016. Application of raw and composted recycled paper mill sludge on the growth of *Khaya senegalensis* and their effects on soil nutrients and heavy metals. *Int. J. Agric. Biol.*, 18: 52–60

yield, quality of the crops and also reduce the N fertilizer requirement (Dayegamiye *et al*., 2013).

Changes in total soil organic carbon (SOC) for different land use and management can be partly explained by the way C is allocated to different fractions of soil organic matter (SOM) (Tan *et al*., 2007). Physical fractionation of SOM is a powerful tool to study the effect of land use change and organic matter turnover in soil. The soil parameter and total organic carbon might not be sensitive to changes in soil quality resulting from relatively recent changes in soil management practices.

Besides being beneficial to plant nutrients, one of the potential hazards of sludge application to agricultural land is the accumulation of heavy metals in crops grown on these soils and groundwater, which can enter the food chain. Thus, the uptake of heavy metals by crops and the fate of these heavy metals in soils should be carefully monitored. Restrictions on sludge application, based on its nutrient content and plant needs are less rigorous, but the recycling practice must ensure that there is no conflict with good agriculture practices, at both national and international levels. Another benefit of these fresh or composted organic materials applications in the different crops is to reduce soil-borne diseases (Darby *et al*., 2006; Olanya *et al*., 2006).

In Malaysia, research on the understanding of crops' responses and the reaction of sludge in acid tropical soils applied with paper mill sludge is significantly lacking. Therefore, studies are required to investigate the factors controlling these responses to crop and soil conditions following application of paper mill sludge produced by paper mills. The benefits of growing crops in a greenhouse have the ability to control all aspects of the growth environment. Hence, this study was conducted to determine the growth response of *Khaya senegalensis*, nutrients uptake and soil status following land application of raw and Recycled Paper Mill Sludge (RPMS) compost under glasshouse conditions. In addition, the study seeks to characterize the physical fractionation of soil organic matter, composed of ^{13}C NMR and FTIR spectra due to application of raw and composted RPMS.

Materials and Methods

Experimental Site and Conditions

The study was conducted in the glasshouse unit at the Faculty of Agriculture, Universiti Putra Malaysia. Bungor Soil Series was used for this study. Some selected physico-chemical properties of the soil, are shown in Table 1. *K. senegalensis* was used as the test crop in 20 and 40 kg polybags arranged in a complete randomized design (CRD). The study was carried out in 4 crop cycles for 1 year growth of *K. senegalensis.* There were eight treatments including the control and 4 replications of each treatment arranged in a complete randomized design (CRD). The treatments were established and presented in Table 2.

Application of Raw and Recycled Paper Mill Sludge Compost and Fertilizer

Paper mill sludge was obtained from United Paper Board Sdn. Bhd., Selangor and composted Recycled Paper Mill Sludge (RPMS) with Empty Fruit Brunch (EFB) at the ratio of 1:1 (RPMS: EFB) was used. Some selected physico-chemical properties of raw and RPMS compost used for the glasshouse experiments are shown in Table 1. The application rates of raw and composted recycled paper mill sludge were applied 0, 150, 300 and 600 kg ha^{-1} at the ratio of 1:1 (Recycled Paper Mill Sludge (RPMS): Empty Fruit Bunch (EFB). Treatments were applied at the beginning of the experiment during transplanting the crops. Healthy seedlings were obtained from the Forest Research Institute Malaysia (FRIM), Kepong, Selangor.

Raw and RPMS compost were air dried and passed through a 2.0 mm sieve and mixed carefully with the soil before filling into the polybags and seedlings were transplanted into polybags. Phosphorous was applied as triple super phosphate (TSP) and potassium as muriate of potash (MOP) both at a rate of 150 kg ha^{-1}.

Crop Maintenance

No chemical pesticides were used in this experiment to avoid heavy metals contamination by these chemical compounds. Weeding was done manually once every fortnight. Water was added daily to retain the soil moisture.

Measurement of Growth Parameters at Harvest

Plant growth parameters (basal diameter and height) were measured every fortnight for the first 6 months and then every month for the next 6 months. Destructive sampling of representative trees was carried out to determine plant nutrients and heavy metal uptake at the end of the study (after 1 year planting). The harvested tree was partitioned into leaves, stems, branch, and roots; and then weighed for dry matter yield content. The samples were dried in an oven (65 – 70°C) until a constant weight was recorded. The dried tissue was ground to pass a 0.1-mm sieve and analyzed for macronutrients and heavy metals.

Soil and Plant Analysis

Determinations of nutrients in the soil and heavy metal concentrations at the end of the study (after 1 year of planting) were carried out. Total N was determined using Kjedahl method (Bremner and Mulvaney, 1982); total organic carbon by combustion technique (Merry and Spounce, 1988) using a CR-412 carbon analyzer (LECO Corporation, St. Joseph, USA). Availablity of P by Bray II method (Bray and Kurtz, 1945), soil exchangeable bases (K^+, Ca^{2+} and Mg^{2+}) were determined (Thomas, 1982), spectra of the raw materials and soil were determined using

FTIR spectroscopy methods of Universal UATR, Model 100 Series Perkin Elmer. Whereas, changes of soil organic matter content were analysed by ^{13}C NMR. The aqua-regia method was used to extract total heavy metals in the sludge and soil (Zarcinas *et al*., 1987) and available heavy metals were extracted by the method by Baker and Michael (1982). Heavy metals in the tissues were determined using the dry ashing method and total N was determined by Kjedahl method (Bremner and Mulvaney, 1982).

Physical Fractionation of Carbon (Density and Particle Size Fractionation)

Soil samples used in this experiment were taken from glasshouse experiment after six and after twelve months of planting. Rates of application of RPMS compost and raw RPMS in the glasshouse experiment were equivalent to the field experiment. There were three treatments in four replicates, namely, a control (no fertilizer), 300 kg N ha^{-1} of RPMS compost and 300 kg N ha^{-1} of raw RPMS. Physical fractionation of organic carbon was carried out on soil based on methods developed by Gaunt *et al*. (2001).

Sequential Extraction Methods

The phase-association forms of heavy metals to the soil components were determined by fractionation (sequential extraction) study. Soil samples used in this study were taken from the glasshouse experiment after one year of the planting. There were four treatments and four replications, which are control (no fertilizer), inorganic fertilizer and 300 kg N ha^{-1} of RPMS compost and 300 kg N ha^{-1} of raw RPMS (the rate was obtained from the previous studies).

Statistical Analyses

All data were analyzed through ANOVA and where found to be significant the means were compared by using a Tukeys' test. Correlation analysis between soil properties and heavy metals in soil and plant parts was performed using Statistical Analyses System (SAS, 2006).

Results

Growth Performance

The growth response of *K. senegalensis* after 1 year of application with raw and composted recycled paper mill sludge showed that the highest rate (600 kg N ha^{-1}) of raw RPMS resulted in the growth of plant height increment to 193 cm. At the same rate, composted recycled paper mill sludge only recorded the height growth of 162 cm (Fig. 1a). The increment was almost two folds higher than that of the control (100 cm). Application of RPMS in its raw form was better than the composted form in improving the plants' height. However, there was no significant difference between the application of raw and composted recycled paper mill sludge after one year of application. Plant growth observation data showed that after 3 months of applying 300 kg N ha^{-1} to *K. senegalensis* using raw and composted RPMS, there was an increment of height and diameter, which is comparable with the inorganic fertilizer.

As expected, the control exhibited the lowest diameter growth for *K. senegalensis* (Fig. 1b). The largest diameter recorded was in treated plot (T5) at 27.00 mm and the lowest was the control plot (T1) at 18.50 mm. After one-year duration, all treatments produced significantly higher than the control for total plant biomass (Fig. 1c). Application of 300 kg N ha^{-1} composted RPMS produced the highest total biomass compared to raw RPMS but the differences were insignificant. Increased plant growth of *K. senegalensis* is probably due to the improved soil physical and chemical properties and increased microbial mineralization activities that led to increase in the availability of macro and micro nutrients in soils after the application of raw and composted paper mill sludge.

Soil Properties in the Soil

The pH, electrical conductivity (EC), available P, total C and CEC in soil varied among the treatments during the planting period. The treatments with raw and RPM compost had higher pH values than those applied with inorganic fertilizer and control (Table 3). Salinity has been measured in terms of the EC of the solution. The EC values indicate whether the treatments would cause any salinity problems to the plants after the sludge treatments. While there was no salinity problem recorded throughout the planting period.

After one year duration, available P in soil treated with raw and RPMS compost was higher than the control in plots grown with *K. senegalensis*. Increase of available P in soil reflects the mineralization of organic P from the decomposition of pulp sludge. There were significant differences (p<0.05) in soil organic carbon content between soil treated with raw (T8) and with RPMS compost (T5) compared to the control. The total carbon increased with increasing rates of sludge applications (Table 3).

Concentration of Macronutrients in the Soil

There was no significant difference in the N content between the treatments with sludge and the control, except for the T5 and T8 treatments grown with *K. senegalensis* (Table 4). The presence of the soil N reserve contributes to part of the N being taken up by the plants. Concentration of N increased in the soil treated with increasing rates of raw and composted RPMS. The composted RPMS application gave the highest N content, whereas there was no significant difference in P concentrations for all treatments. Meanwhile, application of composted RPMS gave higher concentration of K compared to the control.

Table 1: Physico-chemical properties of the soil, raw and RPMS compost used in the glasshouse and field experiment

Parameter	Soil, Depth (0 – 20 cm)	Raw RPMS	RPMS Compost
pH (H_2O)	4.59 ± 0.10	7.84 ± 0.27	7.18 ± 0.44
Total N, (%)	0.14 ± 0.01	4.05 ± 0.26	2.68 ± 0.26
Organic C, (%)	1.36 ±0.62	33.67 ± 4.52	52.52 ± 6.3
Available P, (mg kg^{-1})	14.28 ± 1.12	-	-
Exch. K, (cmol$_{(+)}$ kg^{-1})	0.12 ± 0.01	-	-
Exch Ca , (cmol$_{(+)}$ kg^{-1})	0.85 ± 0.11	-	-
Exch. Mg, (cmol$_{(+)}$ kg^{-1})	1.28 ± 0.21	-	-
CEC, (cmol$_{(+)}$ kg^{-1})	9.55 ± 0.22	28.07 ± 1.25	-
[a]Extr. Cd, (mg kg^{-1})	0.05 ± 0.01	-	-
[a]Extr. Cu, (mg kg^{-1})	1.54 ± 0.20	-	-
Extr. Ni, (mg kg^{-1})	0.45 ± 0.12	-	-
[a]Extr. Pb, (mg kg^{-1})	0.78 ± 0.15	-	-
[a]Extr. Mn, (mg kg^{-1})	1.55 ± 0.60	-	-
[a]Extr. Zn, (mg kg^{-1})	2.58 ± 1.10	-	-
Total Cd, (mg kg^{-1})	0.12 ± 0.02	4.09 ± 0.25	2.48 ± 0.56
Total Cu, (mg kg^{-1})	10.89 ± 1.80	102 ± 2.75	27.71 ± 4.84
Total Ni, (mg kg^{-1})	6.12 ± 0.59	29.11 ± 2.75	20.29 ± 2.32
Total Mn, (mg kg^{-1})	11.15 ± 2.10	329 ± 19	142 ± 23
Total Pb, (mg kg^{-1})	18.59 ± 2.86	328 ± 28	26.94 ± 2.31
Total Zn, (mg kg^{-1})	22.80 ± 2.21	287 ± 22	183 ± 8.9
Bulk density (g cm^{-3})	1.28	-	-
Sand, (%)	61.8	-	-
Silt, (%)	4.6	-	-
Clay, (%)	33.6	-	-
Texture	Sandy clay loam	-	-

[a] Available heavy metals in soil were extracted using 0.1 M HCl
- not detectable, ± standard error, Recycled Paper Mill Sludge (RPMS)

Table 2: The treatments for glasshouse experiment for *K. senegalensis*

No.	Treatments
1	Control (no fertilizer)
2	150 kg N ha^{-1} of inorganic fertilizer (recommended rate)
3	150 kg N ha^{-1} of RPMS compost (1 t ha^{-1} of RPMS compost)
4	300 kg N ha^{-1} RPMS compost (2 t ha^{-1} of RPMS compost)
5	600 kg N ha^{-1} RPMS compost (3 t ha^{-1} of RPMS compost)
6	150 kg N ha^{-1} raw RPMS (0.5 t ha^{-1} of raw RPMS)
7	300 kg N ha^{-1} raw RPMS (1 t ha^{-1} of raw RPMS)
8	600 kg N ha^{-1} raw RPMS (1.5 t ha^{-1} of raw RPMS)

Recycled Paper Mill Sludge (RPMS)

Physical Fractionation of Carbon

Free and Occluded Light Fractions of Carbon

Free and occluded light fractions of the topsoil, were, determined after 6 months and 1 year from *K. senegalensis*. The weight of F-LF and O-LF of soils treated with raw and RPMS compost were significantly different as compared to the control after 6 months and 1 year (Table 5). The F-LF fraction showed a higher dry weight compared to the O-LF. At the 6th month of application of RPMS compost, there was evidence of a significant increase in C concentration in F-LF compared to both RPMS compost and control. However, at 1 year after harvest, raw RPMS compost showed significant increase in C concentration in F-LF compared with RPMS compost and control treatments. This indicates that raw RPMS mineralized at a slower rate than composted RPMS.

Table 3: Soil properties after one year application of composted and raw RPMS

Treatment	pH	EC (µS cm^{-1})	Available P (mg kg^{-1})	Total C (%)	CEC (cmol$_{(+)}$ kg^{-1})
T1	4.57 b	55.4 c	19.11 b	2.28 b	10.93 b
T2	4.75 b	78.2 b	18.62 b	2.30 b	11.29 b
T3	4.89 b	73.6 b	18.18 b	2.35 b	12.11 ab
T4	5.17 a	94.6 a	29.54 a	2.43 b	13.15 a
T5	5.27 a	82.3 a	20.63 ab	2.76 a	12.33 ab
T6	4.76 b	74.0 b	18.10 b	2.39 b	11.28 b
T7	4.92 ab	83.9 a	24.29 ab	2.45 b	13.28 a
T8	5.55 a	68.7 b	22.98 ab	2.98 a	11.90 ab

Means followed by the same letter within a column are not significantly different (p<0.05)

Table 4: Concentrations of macronutrients in soil after one-year application of composted and raw RPMS

Treatment	N	P	K	Ca	Mg
	-------------------------------- %			-----------------------------	
T1	0.34 b	0.10 a	0.013 bc	0.069 b	0.004 b
T2	0.31 b	0.12 a	0.012 bc	0.072 b	0.005 b
T3	0.34 b	0.14 a	0.017 ab	0.072 b	0.005 b
T4	0.36 ab	0.20 a	0.019 ab	0.082 a	0.006 b
T5	0.48 a	0.16 a	0.020 a	0.083 a	0.008 a
T6	0.40 ab	0.15 a	0.015 bc	0.067 b	0.005 b
T7	0.34 b	0.10 c	0.010 c	0.077 ab	0.005 b
T8	0.51 a	0.16 a	0.015 bc	0.082 a	0.005 b

Means followed by the same letter within a column are not significantly different (p<0.05)

Particulate Organic Matter (POM) of Carbon and Nitrogen Concentration

Size fractionation is based on the observation that SOM in sand size fraction (>53 µm), is often more labile than SOM in clay and silt size fractions (Table 6). The results showed that the dry matter content of POM was significant for raw and RPMS compost treatments compared with the control. After 6 months, the application of raw RPMS composts showed significant increase in C and N concentrations compared to both raw RPMS compost and control. After 1 year, there was no significant difference between raw RPMS and RPMS compost. A similar trend was observed in the C/N ratio where there was no significant difference between treatments for harvesting plants at 6 months and 1 year.

Soil Dry Matter Present in Different Size Obtained by Physical Fractionations

The mass proportions of three aggregate size classes in topsoil depth (0–15 cm) varied significantly with the treatments (Table 7). In comparison with control, the application of raw and RPMS compost was dominated by 53–250 µm aggregates followed by the 250–2000 µm, 53 –250 µm and >2000 µm class sizes. In general, soil dry matter in different size of soil fractions obtained by physical fractionation of raw and RPMS compost was higher compared to the control.

Table 5: Free and occluded light fractions of the topsoil after 6 months and 1-year amendment with raw and composted recycled paper mill sludge for glasshouse experiment

Time sampling	Treatment	Free Light Fraction				Intra-aggregate Light Fraction			
		Dry weight ($g\ kg^{-1}$ soil)	C ($g\ kg^{-1}$ soil)	N ($g\ kg^{-1}$ soil)	C/N ratio	Dry weight ($g\ kg^{-1}$ soil)	C ($g\ kg^{-1}$ soil)	N ($g\ kg^{-1}$ soil)	C/N ratio
After 6 months	Control	18.80 c	56.26 b	5.47 b	10.28 a	2.49 b	19.30 b	3.97 b	4.86 b
	RPMS compost	41.99 a	60.27 b	6.27 b	9.61 a	8.99 a	47.18 a	4.91 ab	9.60 a
	Raw RPMS	29.36 b	120.48 a	12.43 a	9.69 a	3.87 b	44.93 a	6.66 a	6.74 ab
After 1 year	Control	10.92 c	139.59 b	7.11 b	19.63 a	8.38 b	11.61 b	1.57 b	7.39 a
	RPMS compost	37.30 a	180.31 a	14.07 a	12.81 ab	19.67 a	73.50 a	7.86 a	6.92 a
	Raw RPMS	19.23 b	120.57 b	12.43 a	9.70 b	14.52 a	67.26 a	6.66 a	5.79 a

Means followed by the same letter within a column are not significantly different ($p<0.05$)

Table 6: SOM sand fraction (> 53 µm) of the topsoil after 6 months and 1-year amendment with raw and composted recycled paper mill sludge

Time sampling	Treatment	Dry weight	C	N	C/N ratio
		------------------ $g\ kg^{-1}$ soil ---------------			
After 6 months	Control	406 b	7.97 b	1.13 b	7.05 a
	RPMS compost	635 a	12.57 a	1.64 a	7.66 a
	Raw RPMS	681 a	9.31 ab	1.26 b	7.38 a
After 1 year	Control	537 b	6.45 b	0.90 a	7.16 a
	RPMS compost	684 a	8.60 a	1.18 a	7.28 a
	Raw RPMS	663 a	9.18 a	1.19 a	7.71 a

Means followed by the same letter within a column are not significantly different ($p<0.05$)

Table 7: Amount of soil dry matter present in the different size soil mineral fraction obtained by the physical fractionations ($g\ kg^{-1}$) of the topsoil after 6 months and 1-year amendment with raw and composted recycled paper mill sludge for glasshouse experiment

Time sampling	Treatment	Size (µm)		
		2000 – 250	250 – 53	53 – 25
After 6 months	Control	198 b	208 b	23.38 b
	RPMS compost	264 a	371 a	27.38 a
	Raw RPMS	287 a	394 a	28.04 a
After 1 year	Control	246 b	291 b	20.91 b
	RPMS compost	299 a	385 a	21.60 ab
	Raw RPMS	282 a	381 a	24.63 a

Means followed by the same letter within a column are not significantly different ($p<0.05$)

Changes of Soil Organic Matter Content by ^{13}C NMR

The quality of ^{13}C NMR spectra after removal of magnetic materials (Fig. 2) showed that addition of compost was able to remove the magnetic materials (Fig. 2a) and has improved the spectral quality and the treatment with bar magnet followed by HF extraction (Fig. 2b). However, the resonance peaks of any type of C structure in the soil remained completely unobservable.

Changes of Soil Organic Matter Content by FTIR

The FTIR spectra of soil treated with raw and RPMS compost compared with the control at day 3 and at 3, 6 and 9 and 12 months after treatments exhibited the same absorbance, indicating that no qualitative changes occur during 1 year of raw and RPMS compost application. However, noticeable changes were observed after 6 months of application where the C-O stretching of phenolic OH (1400–1410 cm^{-1}) was not detected in all treatments. Meanwhile, C≡C substance alkynes (2167 and 2202 cm^{-1}) appeared at the 6th and 12th month, respectively, for raw RPMS treatment, which might be due to the influence of the raw RPMS composition.

Concentrations of Heavy Metals in Soil and Plant Parts of *K. senegalensis*

The application of raw and composted RPMS resulted in significantly higher concentration of Cd compared to the control (Table 8). However, there was no significant difference in Cu, Mn, Ni, Pb and Zn concentrations between treatments.

The Cd was not significantly ($p<0.05$) different in the branch, stem and roots of plants (Table 8). However, the other plant parts (branch, stems and roots) showed that the raw RPMS treatments gave highest concentrations of Cd. Meanwhile, Cu showed no significant difference in the branches of the plants. The other parts showed that the application of raw and RPMS caused lower concentrations of Cu compared to the control. This was probably caused by a decrease in Cu availability because of an increase in soil pH, as well as due to chelation by organic matter. Meanwhile, there was no significant difference ($p<0.05$) of Mn content found in plant parts. Nickel concentration showed significant differences ($p<0.05$) in all plant parts for RPMS compost treatments compared to the control. However, there was no significant difference ($p>0.05$) of Pb content in plant parts of *the K. senegalensis* except for the leaves. Concentrations of foliar Pb were generally higher in raw RPMS and RPMS compost treatments compared to the control. There was no significant difference in Zn concentrations in leaves, stem and branches, although Zn were significantly higher in raw RPMS treatment compared to the control in leaves.

Correlation between Heavy Metals with Soil Chemical Properties and Plant Parts of *K. senegalensis*

Available P was negatively correlated with total Cd in

Table 8: Concentrations of heavy metals in soil and plant parts after one-year application of composted and raw RPMS

Treatment	Cd	Cu	Mn	Ni	Pb	Zn
	--------------------------------		mg kg^{-1}	--------------------------		
Soil						
T1	0.88 b	13.37 a	14.08 a	1.92 ab	13.28 a	36.92 a
T2	2.00 a	16.37 a	14.35 a	2.04 ab	13.91 a	37.16 a
T3	2.33 a	14.64 a	14.35 a	2.41 ab	11.43 a	35.41 a
T4	1.98 a	15.12 a	14.89 a	3.36 ab	12.63 a	38.85 a
T5	2.45 a	15.12 a	16.29 a	4.44 a	12.44 a	38.76 a
T6	2.53 a	14.72 a	15.35 a	1.64 b	12.91 a	36.69 a
T7	2.72 a	15.20 a	14.92 a	0.97 b	13.14 a	39.20 a
T8	2.82 a	13.78 a	14.01 a	0.85 b	11.93 a	34.73 a
Leaves						
T1	0.028 c	7.27 b	28.58 a	1.11 b	3.35 b	41.66 a
T2	0.018 c	8.02 ab	32.57 a	1.27 b	3.19 b	43.92 a
T3	0.046 bc	9.13 ab	38.19 a	1.45 b	3.43 b	49.08 a
T4	0.068 ab	8.22 ab	49.25 a	1.65 b	7.27 ab	44.77 a
T5	0.075 ab	8.07 ab	37.51 a	1.63 b	11.90 ab	45.95 a
T6	0.063 ab	8.21 ab	40.63 a	1.29 b	9.61 ab	52.09 a
T7	0.089 a	8.41 ab	33.02 a	2.08 ab	13.53 ab	54.67 a
T8	0.072 ab	10.28 a	49.69 a	2.82 a	15.93 a	56.81 a
Stem						
T1	0.050 b	5.75 a	12.10 a	0.63 b	1.94 a	65.72 a
T2	0.027 b	7.00 a	16.53 a	0.96 b	2.34 a	53.33 a
T3	0.034 b	5.59 a	12.20 a	1.67 b	2.84 a	59.82 a
T4	0.059 b	6.71 a	14.18 a	1.70 b	3.55 a	79.19 a
T5	0.081 b	6.37 a	14.71 a	1.64 b	2.25 a	66.18 a
T6	0.168 ab	6.03 a	14.50 a	3.79 ab	1.89 a	65.08 a
T7	0.179 ab	6.19 a	10.69 a	6.35 a	2.52 a	63.45 a
T8	0.606 a	6.01 a	16.77 a	6.03 a	2.97 a	64.71 a
Branches						
T1	0.044 a	6.85 ab	6.88 a	0.07 b	0.84 a	41.99 a
T2	0.040 a	7.82 ab	5.23 a	0.78 ab	1.07 a	60.96 a
T3	0.075 a	9.53 a	7.59 a	1.35 ab	1.50 a	79.04 a
T4	0.085 a	8.95 ab	7.95 a	1.91 ab	1.38 a	74.04 a
T5	0.098 a	9.03 ab	10.85 a	2.12 ab	1.49 a	70.08 a
T6	0.049 a	8.14 ab	10.07 a	1.96 ab	2.41 a	74.49 a
T7	0.064 a	6.42 b	8.85 a	2.73 a	1.24 a	68.21 a
T8	0.050 a	7.52 ab	10.86 a	1.42 ab	1.96 a	90.02 a
Roots						
T1	0.037 b	9.05 a	70.46 a	2.36 d	4.40 a	42.98 c
T2	0.136 ab	9.31 a	123.6 a	3.33 dc	6.43 a	59.69 bc
T3	0.308 ab	10.79 a	92.21 a	4.19 bcd	3.97 a	71.49 bc
T4	0.321 ab	10.33 a	126 a	4.44 bcd	6.13 a	58.71 bc
T5	0.345 ab	10.50 a	206 a	4.52 bcd	6.66 a	62.01 bc
T6	0.259 ab	11.05 a	250 a	8.06 a	7.24 a	87.69 ab
T7	0.361 ab	8.81 a	210 a	5.69 abc	7.62 a	107.52 a
T8	0.398 a	9.90 a	209 a	7.00 ab	7.12 a	72.93 b

Means followed by the same letter within a column are not significantly different ($p<0.05$)

soil whereas, total C was positively correlated with available Mn (Table 9). Meanwhile, total Cu shows positive correlation with CEC, which also indicates the affinities of this metal to CEC in soil. This indicates that concentration of Cd, Ni and Pb in soils and soil solutions may enhance the Cd, Ni, Pb concentrations in the leaves. However, available Ni was positively correlated with Ni in the stem. Manganese and Zn concentration in the branches were positively correlated with available Mn and Zn, respectively and Ni in roots was positively correlated with available Ni.

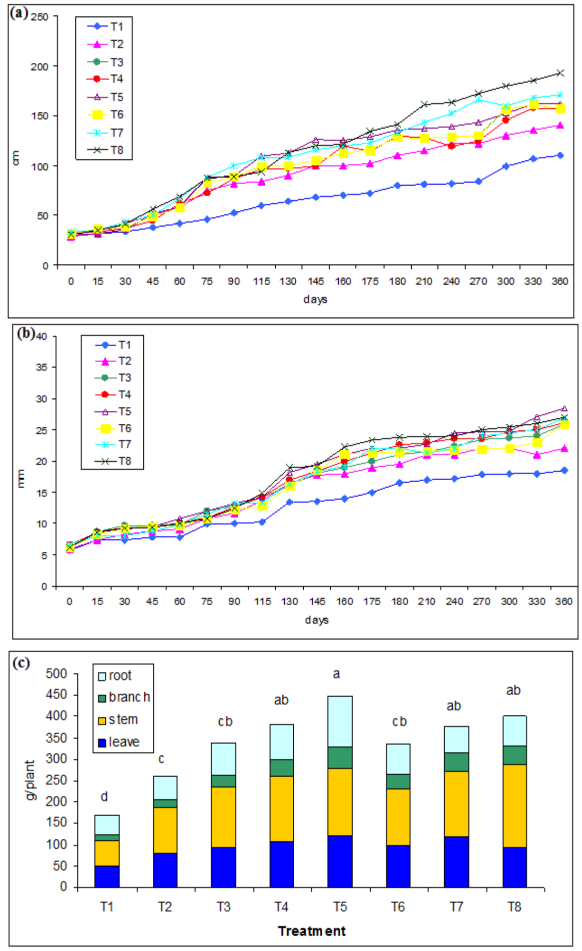

Fig. 1: (a) Height increment (b) diameter growth and (c) plant biomass of *K. senegalensis* after 1 year of application of composted and raw paper mill sludge under glasshouse condition

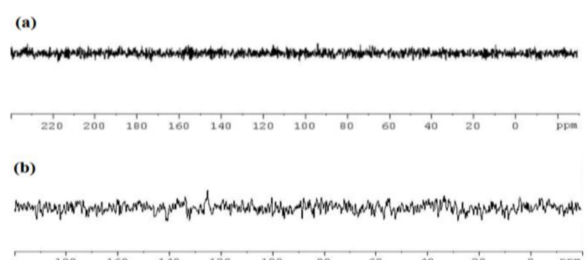

Fig. 2: (a) The ^{13}C NMR spectra without any pre-treatment resulted completely unobservable peaks in spectra (b) The ^{13}C NMR spectra after bar magnet followed by HF treatments

Table 9: Correlation of heavy metals in soil with soil chemical properties and heavy metals content in plant parts of *K. senegalensis*

Heavy metals	Soil Properties					Plant Parts			
	pH	EC	Available P	Total C	CEC	Leave	Stem	Branch	Root
Cd	-0.003 ns	-0.075 ns	-0.457 *	-0.172 ns	-0.312 ns	0.018 ns	0.162 ns	-0.243 ns	-0.123 ns
Cu	0.364 ns	0.181 ns	0.197 ns	-0.233 ns	0.124 ns	-0.065 ns	0.029 ns	-0.467 ns	0.089 ns
Mn	0.024 ns	0.134 ns	-0.058 ns	-0.022 ns	0.191 ns	0.298 ns	0.169 ns	0.272 ns	0.377 ns
Ni	0.003 ns	-0.242 ns	-0.337 ns	0.327 ns	-0.195 ns	0.011 ns	0.326 ns	0.216 ns	0.657 **
Pb	-0.028 ns	0.217 ns	-0.073 ns	-0.235 ns	-0.006 ns	0.310 ns	-0.088 ns	0.279 ns	0.322 ns
Zn	0.158 ns	0.236 ns	0.168 ns	-0.241 ns	0.177 ns	0.552 **	-0.063 ns	0.646 **	0.407 *

Means followed by the same letter within a column are not significantly different (p<0.05)

Discussion

The growth response of *K. senegalensis* with raw and composted recycled paper mill sludge showed the highest N of raw RPMS with highest plant height during the planting period. The addition of the RPMS in its raw form was better than the composted form for the improvement of the plants' height. Farahat and Linderholm (2012) observed similar findings for *K. senegalensis* that can be grown under glasshouse condition and could reach 12.00 mm diameter girth growth within one year. This indicates that the high nutrients in raw and RPMS compost encouraged growth of the saplings. It was observed that the basal diameter of *K. senegalensis* showed a similar trend with the height growth.

Application of biosolid waste from paper mill improved the chemical properties of the soil (Rato *et al*., 2008) and it shows that the pH, EC, available P, total C and CEC in increased soil after one year application of raw and RPMS compost. The high pH in soil contributes to increase yield for a range of crops on acid soils due to the calcium carbonate content of PMS that enhance the soil pH (Sahu and Pal, 1987; Panda and Patttaik, 1990). The increase in soil pH and Ca during the experimental period may have limited effect due to P fixation in the soil (Santos 2003). Furthermore, sludge increased the organic carbon content of soil at the statistically significant for the highest sludge rate (Battaglia *et al*., 2007). However, in this study soil EC values indicated no salinity problems to the plants after the sludge treatments. High salinity (above 4 mS cm^{-1}) will have an adverse effect on plant growth (Ponanperuma and Bradyopadya, 1980).

The N contents between the treatments were not significantly different among the treatments, except for the T5 and T8 treatments grown with *K. senegalensis.* This might be due to presence of the soil N reserve contributing to part of the N being taken up by the plants. The composted RPMS application did not affect the P contents significantly. Meanwhile, application of composted RPMS gave higher concentration of K and Ca compared to the control. According to Rato *et al*. (2008), the Ca in paper mill sludge is a combination of calcium carbonates, hydroxides and oxides reflecting the ingredients used in the paper making process. Therefore, increases in soil pH reflect the dissolution of these alkaline constituents in the sludge over the experimental period.

The concentration of Mg was not significantly increased in the soil applied with composted RPMS. These findings are in the agreement with those of Simard *et al*. (1998) who reported that no consistent trend for soil Mg even with increased paper sludge rates for soil.

Free and occluded light fractions of the topsoil, which were determined after 6 months and 1 year from the *K. senegalensis* plots, varied during the time. The weight of the F-LF and O-LF of soils treated with raw and RPMS compost were significantly different as compared to the control while the F-LF fraction presented a higher dry weight compared to the O-LF. However, after one year, raw RPMS compost showed significant increase in C concentration in F-LF compared with RPMS compost and control treatments. This indicates that raw RPMS mineralized at a slower rate than composted RPMS. According to Owen *et al*. (2008), gains in light fraction of soil organic matter, C and N are expected when soil was amended with compost that contain organic matter in varying stages of transformation from labile fresh material toward humic materials. The C concentration in the O-LF showed significant increase in raw and RPMS compost compared with the control. Nitrogen content of the F-LF and O-LF were statistically affected by the application of raw and RPMS compost after 6 months and 1 year after harvest. The C/N ratio during the study period was not significantly affected. This might be due to the F-LF having greater variation in the concentration of C and N compared to both O-LF. The F-LF has been considered as part of the biologically-active or labile soil organic pool and usually F-LF is enriched in C and N compared to O-LF and the proportion of total C and N may reach 50 and 40%, respectively (Christensen, 1992). Moreover, the paper mill sludge application have enhanced the soil physical and biological properties and improved the N availability (N'Dayegamiye, 2009).

The size fractionation is dependent on the SOM in sand size fraction (>53 µm), and that is mostly more labile than SOM in clay and silt size fractions (Cambardella and Elliot, 1992). The soil amendment prominently improved the dry matter content of POM. This was due to more nutrient availability as well as nutrient uptake that may enhance the dry weight. Additionally, the soil dry matter in different soil fractions obtained by the physical fractionations of raw and RPMS compost was higher compared to the control.

Solid State ^{13}C NMR has been recognized as one of the techniques to effectively characterize the soil organic matter. A major advantage of the solid-state ^{13}C NMR technique is the possibility of obtaining the structural information of the soil organic matter in bulk soils or solid fractions without the necessity of extracting the organic material. However, the prerequisite to acquire a good NMR spectrum is to remove the paramagnetic substances from the samples (Wilson, 1987). The major problem in ^{13}C NMR studies of soil organic matter is the low C in soils. Long acquisition times, low resolution and low signal-to-noise ratios of the spectra are common when conducting ^{13}C NMR studies of soil organic matter in soils with low C. It is quite difficult to acquire an acceptable signal-to-noise ratio of ^{13}C NMR spectrum of C contents of 5 g kg^{-1} or below (Kögel-Knabner, 1997). The FTIR spectra of treated soil with raw and RPMS compost compared with the control showed the same absorbance which, indicated that no qualitative changes occurred during the study period however, obvious changes were reported after 6 months where the C-O stretching of phenolic OH was not noticed which might be due to the influence of the raw RPMS composition (Kögel-Knabner, 1997).

The addition of paper mill sludge to soil induced a decrease in the mobile forms of Zn and Pb, probably due to the presence of organic matter and kaolinite in sludge, which were able to bind the metal strongly (Battaglia *et al.*, 2007). On other side, total concentrations of Cu, Ni, Pb and Zn in soil after application of raw and composted RPMS were lower in concentration with the Investigation Level for Malaysian soils which the level is taken at the 95th percentile of the heavy metals data for agricultural soils (Zarcinas *et al*., 2004). Soils with values over this 95th percentile will be regarded as contaminated. However, the concentration of Cd exceeded the Investigation Level of 0.3 mg kg^{-1} for Malaysian soils, but below the Australian Ecological Investigation Level (EILs) of 3 mg kg^{-1}. The concentration of heavy metals in soil amended with paper mill biosolids or plant grown in these soils have usually been below established standards observed by several researchers (Baziramakenga and Simard, 2001). Furthermore, the concentration of heavy metals were not shown the differences except at Pb of raw and RPMS compost compared with the control. Zinc concentrations in leaves, branches and roots were positively correlated with total Zn. Cd in leaves was positively correlated with available Cd, Ni and Pb. This indicates that concentration of Cd, Ni and Pb in soils and soil solutions may influence Cd, Ni, Pb concentrations in the leaves. Meanwhile, available Ni was positively correlated with Ni in the stem. Manganese and Zn concentration in the branches were positively correlated with available Mn and Zn, respectively and Ni in roots was positively correlated with available Ni.

Conclusion

Total concentrations of Cu, Ni, Pb and Zn in soils are below the Investigation Level for Malaysian Soils, which is at the 95th percentile of heavy metals data for agricultural soils. Meanwhile, the concentration of Cd was below the Australian Ecological Investigation Level (EILs) of 3 mg kg^{-1}. Concentrations of heavy metals in leaves were under the MPC value of the Malaysian Food Act 1983 and Food regulation 1985. This research also demonstrated that paper mill sludge could be successfully used as a soil amendment and fertilizer in acidic soil without any adverse effect. Both the materials were safe for mulching and fertilizing of edible plants and forest trees. The use of paper mill sludge’s to improve soil fertility through land application represents a unique opportunity to recycle sludge back to the land while alleviating a potential waste management problem.

Acknowledgement

The authors acknowledge Universiti Putra Malaysia, University of Malaya and the Ministry of Science, Technology and Innovation Malaysia for financial and technical support for this study.

References

Baker, D.E. and C.A. Michael, 1982. Nickel, copper, zinc and cadmium. *In: Methods of soil analysis*. 2nd edition. pp: 323-336, Part 2. Chemical and Microbiological Properties

Battaglia, A., N. Calace, E. Nardi, B. Petronio and M. Pietroletti, 2007. Reduction of Pb and Zn bioavailable forms in metal polluted soils due to paper mill sludge addition. Effect on Pb and Zn transferability to barley. *Bioresource Technol*., 98: 2993–2999

Baziramakenga, R. and S.S. Simard, 2001. Effect of de-inking paper sludge compost on nutrient uptake and yields of snap bean and potatoes grown in rotation. *Compost Sci*., 9: 115–126

Bray, R.H. and L.T. Kurtz, 1945. Chemical analysis: Phosphorus., *In*: *Soil Survey Laboratory Staff* (Eds). pp: 321–325, Soil Survey Laboratory Method Manual. Washigton: USDA

Bremner, J.M. and C.S. Mulvaney, 1982. Nitrogen-total. *In*: *Methods of Soil Analysis*. pp: 595–622, A.L., Miller R.H. and D.R. Keeney (eds.). Proc. Chemical and Microbiological Properties, Agronomy Monograph., 9., American Society of Agronomy, Madison, WI

Cambardella, C.A. and E.T. Elliot, 1992. Particulate soil organic matter changes accross a grassland cultivation sequence. *Soil Sci. Amer. J*., 56: 777–783

Catricala, C.E., W.B. Bowden, C.T. Smith and W.H. McDowell, 1996. Chemical characteristics of leachate from pulp and paper mill residuals used to reclaim a sandy soil. *Water Air Soil Pollut*., 89: 167–187

Christensen, B.T., 1992. Physical fractionation of soil and organic matter in primary size and density separates. *Adv. Soil Sci*., 20: 1–90

Darby, H.M., A.G. Stone and R.P. Dick, 2006. Compost and manure mediated impacts on soil borne pathogens and soil quality. *Soil Sci. Amer. J*., 70: 347–358

Farahat, E. and H.W. Linderholm, 2012. Ecological impacts of desert plantation forests on biodiversity. *Afr. J. Ecol*., 50: 308–318

Gaunt, J.L., S.P. Sohi, H. Yang, N. Mahieu and J.R.M. Arah, 2001. A procedure for isolating organic matter fractions suitable for modelling, R.M. *et al*., (eds.). *Sustainable management of soil organic matter*. pp: 90–95, CABI Publishers, New York, USA

Jean, M.R. and R. Santosh, 2006. Feeding China's Expanding Demand for Wood Pulp: A Diagnostic Assessment of Plantation Development, Fiber Supply and Impacts on Natural Forests in China and in the South East Asia Region. Pages 28 in Malaysia Report. Center for International Forestry Research, Malaysia

Kögel-Knabner, I., 1997. ^{13}C and ^{15}N NMR spectroscopy as a tool in soil organic matter studies. *Geoderma*, 80: 243–270

Lacour, P., 2005. Pulp and paper markets in Europe. Prepared for the United Nations Economic Commission for Europe and the Food and Agriculture Organization of the United Nations. USA

Merry, R.H. and L.S. Spouncer, 1988. The measurement of carbon in soils using a microprocessor-controlled resistance furnace. *Commun. Soil Sci. Plant Anal*., 19: 707–720

Miner, R., 1991. *Environmental Considerations and Information Needs Associated With an Increased Reliance on Recycled Fiber*. pp: 343–362, in Focus 95$^+$ Proceedings, TAPPI PRESS, Atlanta

N'Dayegamiye, A., 2009. Soil properties and crop yields in response to mixed paper mill sludges, dairy cattle manure, and inorganic fertilizer application. *Agron. J*., 101: 826–835

N'Dayegamiye, A., J. Nyiraneza, M. Giroux, M. Grenier and A. Anne Drapeau, 2013. Manure and Paper Mill Sludge Application Effects on Potato Yield, Nitrogen Efficiency and Disease Incidence. *Agronomy*, 3: 43–58

Olanya, O.M., D.H. Lambert and G.A. Porter, 2006. Effects of pest and soil management systems on potato diseases. *Amer. J. Potato Res*., 83: 397–408

Owen, J., D. Lynch and D. Fillmore, 2008. *Changes in Light Fraction Soil Organic Matter and in Organic Carbon and Nitrogen in Compost Amended Soils*. 16th IFOAM Organic World Congress, Modena, Italy

Panda, D. and R.N. Pattnaik, 1990. Effect of different sources of phosphorous and levels of lime on groundnut. *Ind. J. Agron*., 35: 426–427

Ponanperuma, F.N. and A.K. Bradyopadya, 1980. *Soil Salinity as Constrain on Food Production in the Humid Tropics*. pp: 203–216 in Soil related constrain to food Production in the Tropics. IRRI, Los Banos, Philippine

Rato, J., A. Nutes, F. Cabral and B.A. Lopez-Pineiro, 2008. Short-term effect on soil properties and wheat production from secondary paper sludge application on two Mediterranean agricultural soils. *Bioresour. Technol*., 99: 4935–4942

Sahu, S.K. and S.S. Pal, 1987. Direct and residual effect of paper mill sludge and lime stone on crop yield under three different crop rotation on an acid red soil. *J. Ind. Soc. Soil Sci*., 35: 46–51

Santos, J.Q., 2003. *Fertilização-fundamentos da utilização de adubos ecorrectivos*. p: 441, Europa-America, Colecçao Euroagro, Lisboa

Simard, R.R., J. Coulombe, R. Lalande, B. Gagnon and S. Yelle, 1998. *Use of Fresh and Composted De-inking Sludge in Cabbage Production*. pp: 349–361, S., Andle, J.S. and Jacob, L. (eds.) Beneficial co-utilization of agricultural, municipal and industrial by-product. Kluwer Academic Press, Dordrecht, The Netherlands

Tan, Z., R. Lal, L. Owens and R.C. Izaurralde, 2007. Distribution of light and heavy fractions of soil organic carbon as related to land use and tillage practice. *Soil Till. Res*., 92: 53–59

Thomas, G.W., 1982. Exchangeable cations. *In*: *Methods of Soil Analysis*. pp: 159–165, Chemical and Microbiological Properties-Agronomy. Page, A.L., Miller, R.H. and Keeney, D.R. eds. Monograph No. 9 (2nd edition). American Society of Agronomy, Madison, Wisconsin, USA

Vasconcelos, E. and F. Cabral, 1993. Use and Environmental Implications of Pulp-Mill Sludge as an Organic Fertilizer. *Environ. Pollut*., 80: 159–162

Wilson, M.A., 1987. *NMR Techniques and Application in Geochemistry and Soil Chemistry*. Pergamon Press, Oxford, UK

Zarcinas, B.A., B. Cartwright and L.R. Spouncer, 1987. Nitric acid digestion and multi-element analysis of plant material by inductively coupled plasma spectrometry. *Commun. Soil Sci. Plant Anal*., 18: 131–146

Zarcinas, B.A., I. Che Fauziah, M.J. McLaughlin and G. Cozens, 2004. Heavy metals in soils and crop in Southeast Asia. Environ. *Geochem. Health*., 26: 343–357

(Received 29 January 2015; Accepted 09 June 2015)